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Exaggerated grain growth in Ni-doped BaTiO$_3$ ceramics

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Abstract

With approximately 0.7 mol% Ni doping, the formation of hexagonal phase in BaTiO$_3$ after sintering at a temperature above 1385 °C in air has been observed. The shape of the h-BaTiO$_3$ grains is plate-like, and the length of these h-BaTiO$_3$ plates can be longer than 15 mm. As the amount of Ni doping increases above or decreases below 0.7 mol%, the hexagonal phase disappears and the resulting microstructure is dominated by small BaTiO$_3$ grains. This critical amount of Ni (i.e. 0.7 mol%) corresponds to the solubility of Ni in BaTiO$_3$. The exaggerated growth of the plate-like grains in BaTiO$_3$ relates strongly to the formation of oxygen vacancies due to the presence of Ni acceptors.
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1. Introduction

Barium titanate (BaTiO$_3$) is a ferroelectric material with high permittivity. The phase of BaTiO$_3$ at room temperature is a tetragonal phase, then transforms to cubic phase at 130 °C [1]. The phase transformation from cubic phase to tetragonal phase has received wide attention for its correlation with the ferroelectric characteristics of BaTiO$_3$. Apart from cubic and tetragonal phases, BaTiO$_3$ can also be present as other crystalline forms. For example, a hexagonal phase is stable at a temperature higher than 1460 °C [1]. However, the attention given to the phase is relatively little.

Several studies indicated that the h-phase could be formed by sintering BaTiO$_3$ in a reducing atmosphere [2]; or by doping acceptors, such as Mg, Al, Cr, Mn, Fe, Co, Zn, Ga, Ni, In, Cu, etc. [3–7]. The vacancy concentration within BaTiO$_3$ increases with the decrease of oxygen partial pressure in the sintering atmosphere [8]. The addition of acceptors also induces the formation of vacancies [9]. To increase the concentration of oxygen vacancy is the key to the formation of hexagonal phase. A recent study indicated that polycrystalline h-BaTiO$_3$ could be used as microwave component [10]. However, the microwave characteristics of h-BaTiO$_3$ single crystal are not yet available. It is therefore of interest to prepare the h-BaTiO$_3$ single crystal.

Tetragonal BaTiO$_3$ tends to form large grains with equiaxed features at elevated temperatures, especially when a small amount of Ti-rich phase is present [11]. Many researchers had taken the advantage of this behavior to produce large BaTiO$_3$ single crystal by using pressureless sintering. The dimensions of t-BaTiO$_3$ single crystal can reach 10 mm [12].

The shape of h-BaTiO$_3$ grains is plate-like [13]. However, the size of such h-phase grains depends strongly on the sintering atmosphere and the amount of acceptors. To the best knowledge of the present authors, the size of the h-BaTiO$_3$ grains can be produced by pressureless sintering in previous studies is less than 150 μm.

The objective of the present study is to produce large h-BaTiO$_3$ grains by using pressureless sintering in air. In order to achieve this target, a small amount of NiO is added into BaTiO$_3$. The processing conditions to produce such large h-phase grains are reported here. The electrical properties of the h-BaTiO$_3$ single crystal will be discussed in a separate report.

2. Experimental procedure

Barium titanate powder (NEB, Product No. 52909, Ferro Co., USA) and various amount of nickel nitrate (ACROS Organics Co., USA) were tumble milled together in ethyl alcohol for 4 h. The Ba/Ti ratio of the BaTiO$_3$ powder as reported by the manufacturer was 1.000 ± 0.002. The total amount of other impurities (SrO $\sim$ 150 ppm, CaO $\sim$ 20 ppm, Fe$_2$O$_3$ $\sim$ 70 ppm, SiO$_2$ $\sim$ 75 ppm, Al$_2$O$_3$ $\sim$ 75 ppm) was less than 400 ppm. The grinding media used was zirconia balls. The slurry of the powder mixtures was dried using a rotary evaporator. The dried lumps were then crushed and passed through a plastic sieve. The powder was calcined in air at 500 °C for 2 h to remove the nitrate; then the

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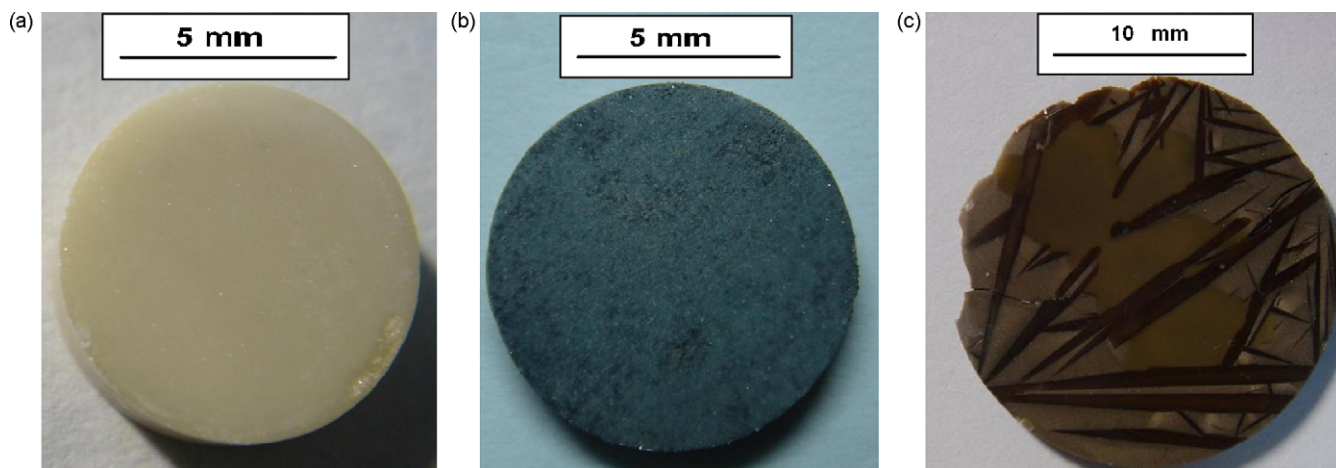*E-mail address:* tuan@ccms.ntu.edu.tw (W.H. Tuan).

Fig. 1. Morphology of BaTiO$_3$ (a and b) and Ni-doped BaTiO$_3$ (c) specimens after sintering at 1400 °C in air for 2 h. The BaTiO$_3$ in (b) was sintered in a flowing H$_2$/N$_2$.

powder was sieved again. The powder was formed into disks by pressing uni-axially at 25 MPa. The size of the discs was 10 mm in diameter and about 3 mm in thickness. The sintering was performed in air at 1330–1400 °C for 2 h. The heating and cooling rates were 3 °C min^{-1}. For comparison purpose, several BaTiO$_3$ specimens were also prepared and sintered in a flowing gas mixtures of nitrogen (95%) and hydrogen (5%).

The density was determined by the water displacement method. The polished specimens were prepared by grinding with SiC particles and polishing with Al$_2$O$_3$ particles. The grain boundary was revealed by etching with a dilute solution of HCl and HF or by etching thermally at a temperature 100–120 °C below the sintering temperature for 30 min. The microstructure was observed by an optical microscope (OM) or a scanning electron microscope (SEM). The grain size was determined by applying an image analysis technique on the photos taken from OM or SEM. Phase identification was performed by X-ray diffractometry (XRD) at a scanning rate of 0.05° 2θ s^{-1}. A very slow scanning rate (0.002° 2θ s^{-1}) was also used to determine the lattice constants of c and a by using the (0 0 2) and (2 0 0) reflections. The c/a ratio was then obtained.

3. Results

XRD analysis reveals only tetragonal BaTiO$_3$ and NiO in the powder after the calcination at 500 °C. Fig. 1(a) and (b) show the surface of the BaTiO$_3$ samples after sintering at 1400 °C in air. The color of BaTiO$_3$ specimen, Fig. 1(a), is light brownish after sintering. However, the color of the BaTiO$_3$ specimen sintered in an oxygen-lean environment (flowing H$_2$/N$_2$) is dark blue (see Fig. 1(b)). The color of Ni-doped BaTiO$_3$ specimen is also very dark after sintering in air (Fig. 1(c)). Several large grains are long enough to spread across the entire cross-section of the disc. The maximum length of such large grains is around 15 mm, which is close to the diameter of the disc.

Fig. 2 shows the XRD patterns of BaTiO$_3$ and Ni-doped BaTiO$_3$ specimens after sintering at 1330 °C and 1400 °C in air. Only tetragonal phase is found in the BaTiO$_3$ specimens. After the addition of 0.7 mol% Ni, the tetragonal phase remains the only phase present in the specimen sintered at 1330 °C. However, a hexagonal phase is found as the major phase in the Ni-doped BaTiO$_3$ specimen as the sintering temperature is raised to 1400 °C. Furthermore, a small amount of Ba$_6$Ti$_{17}$O$_{40}$ (B6) phase is also found.
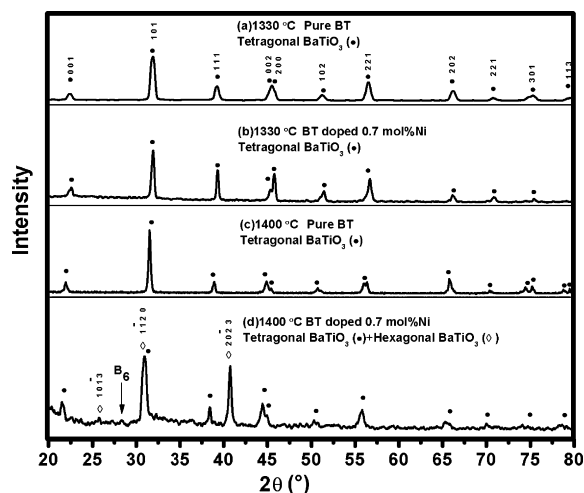

Fig. 2. XRD patterns of BaTiO$_3$ and Ni-doped BaTiO$_3$ specimens after sintering at 1330 °C or 1400 °C.

The values of c/a ratio are shown as a function of Ni content in Fig. 3. The ratio drops from 1.010 to a lower value of 1.004 as the Ni content is higher than 0.7 mol%, then stabilize at 1.004 with the further increase of Ni content. It indicates that Ni^{2+} ion
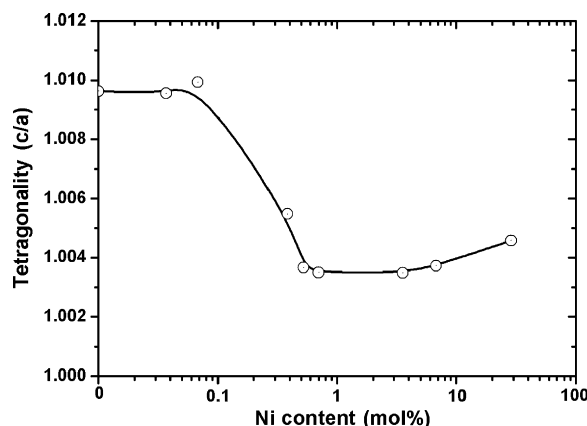

Fig. 3. Tetragonality (c/a ratio) of tetragonal BaTiO$_3$ as a function of Ni content.